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Plastics — Determination of permanganate absorption number of caprolactam — Spectrometric method

Plastiques — Détermination de l'indice d'absorption de permanganate du caprolactame — Méthode spectrométrique

Reference number
ISO 8660:2002(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 8660 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This second edition cancels and replaces the first edition (ISO 8660:1988), which has been technically revised.

Introduction

The permanganate index, expressed as the permanganate absorption number (PAN), defines the stability of a caprolactam sample to potassium permanganate in a buffered neutral aqueous solution and is a measure of the purity of the caprolactam in relation to the presence of oxidizable impurities, e.g. unsaturated caprolactams.

Permanganate in a neutral aqueous solution is a strong oxidizing agent, capable of oxidizing the impurities in caprolactam. The determination of the permanganate absorption number is based on measurement of the absorbance of a 3 % (by mass) aqueous caprolactam solution at a wavelength of 420 nm. The measurement is carried out 10 min after adding a potassium permanganate solution of 0,002 mol/l. To correct for the oxidation of water, a blank determination is carried out.

In general, the oxidation reaction with unsaturated organic compounds is faster than with saturated organic compounds. Unsaturated caprolactam is oxidized at a faster rate than saturated caprolactam. The reaction speed depends upon the reducing agent and, in addition to other experimental conditions, strongly on the pH of the solution. The majority of the unsaturated impurities in caprolactam are considered to react within a period of 10 min. The reaction does not end there, however, as the oxidation of slowly oxidizing compounds, e.g. caprolactam, will continue.

The amount of manganese dioxide generated during the reaction is determined at a wavelength of 420 nm. The contribution of caprolactam at this wavelength in the method described here is less than 0,2 % of the total absorbance.

The method is sensitive to external factors and therefore needs to be followed closely. The results obtained with the method in this edition of ISO 8660 are approximately 11 % lower than those obtained with ISO 8660:1988. The difference is due to buffering of the test solution and the blank at pH 7,0. Buffering the solution at a pH of 7,0 results in a significantly higher precision of the method, as fluctuations caused by the acidity/alkalinity of the sample are eliminated.

Plastics — Determination of permanganate absorption number of caprolactam — Spectrometric method

WARNING — This International Standard may involve hazardous chemicals, materials or operations. This standard does not purport to address the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish proper safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a spectrometric method for the determination of the permanganate absorption number of caprolactam for industrial use. The permanganate absorption number is a measure of the oxidizable impurities in caprolactam, determined in a buffered neutral aqueous medium under fixed conditions.

The method is applicable to purified caprolactam (and intermediates in the caprolactam purification process) with an alkalinity or acidity lower than 0,50 mmol/kg and a PAN value of up to 35.

2 Term and definition

For the purposes of this International Standard, the following term and definition apply.

2.1

permanganate absorption number

PAN

index based on measurement of the absorbance at 420 nm of a 3 % (by mass) buffered neutral aqueous caprolactam solution in comparison with a blank consisting of buffered water, after addition of a standard solution of potassium permanganate, $c =$ 0,002 mol/l, to each and allowing each to stand for 10 min, the absorbance being measured in a cell of pathlength 5 cm

NOTE The PAN is the difference between the absorbance of the test solution and that of the blank, multiplied by 100/3 for a glass cell of pathlength 5 cm.

3 Principle

Equal amounts of potassium permanganate are added to a buffered caprolactam test solution and to a blank consisting of buffered water. After a reaction time of 10 min, the absorbance at a wavelength of 420 nm of the caprolactam test solution and the blank are compared in glass cells with a pathlength of 5 cm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade or of the grade specified.

4.1 Sulfuric acid, p.a., 95 % (by mass) to 97 % (by mass).

4.2 Hydrochloric acid, p.a., 37 % (by mass).

4.3 Oxalic acid dihydrate, $c =$ 0,1 mol/l.

4.4 **Millipore-Q** (or **double-distilled**) **water**.

4.5 **pH 7,0 buffer salt**, exclusively composed of potassium dihydrogen phosphate (40,30 %) and disodium hydrogen phosphate (59,70 %). The salt shall not contain impurities that influence the PAN analysis.

Some commercially available buffer salts contain impurities and/or preservatives which influence the PAN analysis. The suitability of a commercially available buffer salt shall always be tested by comparing the PAN results obtained with this buffer salt with those obtained with a buffer salt made of analytically pure components. The maximum storage time of a commercially available buffer salt or the pure components shall never be exceeded.

4.6 pH 7,0 buffer solution.

Dissolve 3,3 g of the buffer salt (4.5) in Millipore-Q water (4.4) in a 500 ml volumetric flask and make up to the mark with Millipore-Q water. This solution shall be discarded 6 months after preparation (or sooner if any sediment is noticed).

4.7 PAN water.

Add 2,5 ml/l of buffer solution (4.6) to a small quantity of Millipore-Q water in a 1 l volumetric flask, make up to the mark with Millipore-Q water and degas with helium (4.11). Prepare a fresh solution daily. The PAN value of a blank determination shall be $<$ 0,67.

4.8 **Potassium permanganate**, solid, p.a.

4.9 **Potassium permanganate stock solution**, $c =$ 0,020 mol/l.

Store in a brown bottle in the dark. Prepare a fresh solution every 4 weeks. Check the solution every day for manganese dioxide deposit on the walls of the bottle (see the note to 7.1). If any deposit is observed, the solution shall be discarded.

4.10 **Potassium permanganate solution**, $c =$ 0,002 mol/l.

Store in brown bottle in the dark. Prepare a fresh solution weekly from the 0,020 mol/l potassium permanganate solution (4.9). Before use check the solution for manganese dioxide deposit on the walls of the bottle. If any deposit is observed, the solution shall be discarded.

4.11 Helium.

5 Apparatus

Ordinary laboratory apparatus and additionally:

5.1 **Spectrometer**, suitable for monochromatic analyses at 420 nm, bandwith $\leqslant$ 2 nm.

5.2 **Glass cells**, pathlength 5 cm.

5.3 **Water bath**, capable of being maintained at 25,0 $^\circ$C $\pm$ 0,5 $^\circ$C.

5.4 **Stopwatch**, accurate to at least 0,5 s.

5.5 **Glassware**, extremely clean and suitable for PAN analyses (see 7.1).

NOTE Disposable syringes and other plastic devices are not suitable because of the extraction capacity of caprolactam. Additives extracted from plastic devices such as syringes have a negative effect on the PAN determination.

5.6 **Pipette**, made of glass (e.g. a Pasteur pipette), chemically clean (see 7.1).

NOTE Plastic pipettes are not suitable (see note to 5.5).

6 Sample

Caprolactam samples shall be stored in chemically clean, preferably glass, containers. If plastic flasks or containers are used, contact with hot, liquid caprolactam shall be avoided. Caprolactam solutions shall not be stored in plastic containers and any contact with e.g. plastic stoppers shall be avoided (see 5.5).

Samples can consist of pure solid caprolactam or caprolactam solutions. The preferred sample is a solution containing 50 % (by mass) of caprolactam in Millipore-Q water.

NOTE Sampling of pure liquid caprolactam may result in an increase in the PAN value, as a result of oxidation of caprolactam in the presence of air.

7 Procedure

7.1 Cleaning of the glassware

Glassware used for the first time in PAN analysis shall be cleaned successively with

- concentrated sulfuric acid (4.1),
- tap water,
- concentrated hydrochloric acid (4.2),
- Millipore-Q water (4.4).

Glassware used for PAN analysis shall be used for that purpose only and shall be cleaned at least once every 6 months using the above procedure.

Glassware shall be rinsed with tap water (3 times) immediately after the analysis, followed by rinsing 3 times with Millipore-Q water (4.4). Glassware shall be stored closed.

NOTE If the glassware is not rinsed immediately after the analysis, manganese dioxide will settle on the inside surface of the glass. Manganese dioxide catalyses the reaction and has a negative effect on the PAN determination. Manganese dioxide can be removed from the glassware by rinsing with oxalic acid (4.3).

7.2 Purity of the PAN water

Check the PAN water (4.7) by carrying out a blank determination in accordance with 7.3 and calculate its PAN value (see clause 8). If the PAN value is $<$ 0,67, the PAN water is acceptable.

For e.g. production control, the blank determination carried out to check the PAN water should preferably be combined with a determination carried out on a control sample. Analysis of further samples should only be carried out if both the blank and the control sample meet the specifications.

If the PAN value of the PAN water is $>$ 0,67, repeat the blank determination with a freshly prepared 0,002 mol/l solution of potassium permanganate (4.10) and, if necessary, a fresh 0,020 mol/l stock solution of potassium permanganate (4.9).

If the PAN value is still $>$ 0,67, purify the Millipore-Q water by dissolving 1 g of potassium permanganate (4.8) in each litre of Millipore-Q water, storing the solution for 24 h and then distilling with a 600 mm Vigreux column, collecting the first three-quarters of the solution to distill over. Use this purified Millipore-Q water to prepare a fresh solution of PAN water.

If the PAN water still does not meet the specification of $<$ 0,67 PAN units (for a glass cell of 5 cm in length, this corresponds to an absorbance of 0,020), the potassium permanganate may be contaminated with manganese dioxide or the PAN water may have too high an impurity content.

7.3 Determination

Weigh 3,00 g ± 0,03 g of solid caprolactam or 6,00 g ± 0,06 g of 50 % (by mass) caprolactam solution in Millipore-Q water into a 100 ml volumetric flask, transferring the solution with a glass pipette. If the concentration of the caprolactam solution is not 50 %, determine the mass of the test portion by dividing 3,0 g by the concentration of the caprolactam solution, expressed as a percentage by mass, and multiplying by 100. In the case of solid caprolactam, add 50 ml of PAN water (4.7) and dissolve the caprolactam. Make up to the mark with PAN water and mix. Place the flask in a water bath at 25,0 °C ± 0,5 °C for at least 15 min. Add 2,00 ml of permanganate solution (4.10) and start the stopwatch immediately. Mix carefully, minimizing the amount of oxygen entering the mixture, and put the flask back in the water bath. After 9 min, fill two glass spectrometer cells with the test solution and with Millipore-Q water, respectively. Determine the absorbance of the solution after 10 min ± 10 s in comparison with the Millipore-Q water at a wavelength of 420 nm.

The reaction time is critical as slowly oxidizing components, e.g. caprolactam, will continue to react. The test solution shall only be exposed to the light source of the spectrometer during the last minute of the reaction time. A spectrometer provided with a chopper is preferred.

Carry out a blank determination in the same way. Measure the absorbance of the blank directly after that of the test solution but allowing the same reaction time of 10 min ± 10 s.

If the absorbances of e.g. a series of test solutions are measured and/or the absorbances of the test solution and the blank are not measured in direct succession, the drift of the spectrometer shall not exceed 0,1 % of full scale during the total length of time. The specification for PAN water is $< 0{,}67$ PAN units, which corresponds, for a glass cell of 5 cm in length, to an absorbance of $< 0{,}020$. For a glass cell of 5 cm in length and a difference in time of 10 min between the first measurement and the last measurement of a series, the drift of the spectrometer shall not exceed $0{,}02 \times 0{,}1\ \% = 0{,}000\,02$ absorbance units/10 min $= 0{,}000\,12$ absorbance units/h.

8 Calculation

Calculate the permanganate absorption number (PAN) using the formula

$$\text{PAN} = (A_1 - A_0) \times \frac{100}{3}$$

where

A_1 is the absorbance of the test solution in comparison with Millipore-Q water;

A_0 is the absorbance of the blank solution in comparison with Millipore-Q water.

9 Precision

The reproducibility of this method is not known because inter-laboratory data are not available. However, the reproducibility is expected not to deviate significantly from the estimated reproducibility given in Table 3. Inter-laboratory data are being obtained and will be added at the next revision.

Repeatability data, however, have been determined within one laboratory by ninefold analysis of six caprolactam samples on two separate occasions. This was done using the method in ISO 8660:1988 and also using the method in this edition (i.e. with the test solutions buffered at pH 7,0). Results are given in Tables 1 and 2.

For PAN values between 0,6 and 10, the repeatability of the buffered method specified in this edition of ISO 8660, expressed as coefficient of variation, can be seen to lie between 0,7 % and 2,3 %.

Reproducibility data for the buffered method specified in this edition of ISO 8660 have been estimated by analysis of a 50 % caprolactam solution over a longer period of time and with two laboratories involved.

For PAN values around 3,5, the reproducibility of the buffered method specified in this edition of ISO 8660, expressed as the coefficient of variation, is expected to lie between 4,5 % and 5,5 %.

Table 1 — Repeatability data for first set of analyses

Parameter[a]	Caprolactam sample											
	1		2		3		4		5		6	
	Edition of ISO 8660 used											
	2002	1988	2002	1988	2002	1988	2002	1988	2002	1988	2002	1988
x	0,60	0,68	4,39	4,45	3,89	4,87	6,04	7,24	8,59	9,99	10,49	10,76
s_r	0,01	0,03	0,06	0,16	0,07	0,24	0,07	0,15	0,06	0,28	0,10	0,36
CV	2,3	4,4	1,5	3,6	1,8	4,9	1,2	2,1	0,7	2,8	0,9	3,3

For the method specified in this edition of ISO 8660, x was varied between 0,60 and 10,49.

[a] The meanings of the parameters are as follows:

x is the mean PAN value;

s_r is the repeatability standard deviation of the mean;

CV is the repeatability coefficient of variation.

Table 2 — Repeatability data for second set of analyses

Parameter[a]	Caprolactam sample											
	1		2		3		4		5		6	
	Edition of ISO 8660 used											
	2002	1988	2002	1988	2002	1988	2002	1988	2002	1988	2002	1988
x	0,65	0,70	4,46	5,12	3,73	4,33	6,17	7,21	8,72	9,06	10,36	11,49
s_r	0,01	0,03	0,05	0,29	0,07	0,19	0,12	0,40	0,10	0,14	0,11	0,32
CV	1,1	4,2	1,1	5,7	1,8	4,3	2,0	5,5	1,2	1,5	1,1	2,7

For the method specified in this edition of ISO 8660, x was varied between 0,65 and 10,36.

[a] The meanings of the parameters are as follows:

x is the mean PAN value;

s_r is the repeatability standard deviation of the mean;

CV is the repeatability coefficient of variation.

Table 3 — Estimated reproducibility data

Parameter[a]	Laboratory 1	Laboratory 2
x	3,57	3,38
s_R	0,20	0,15
CV	5,5	4,5
Number of analyses	37	22
Number of analysts	$>$ 10	3

[a] The meanings of the parameters are as follows:

x is the mean PAN value;

s_R is the reproducibility standard deviation of the mean;

CV is the reproducibility coefficient of variation.

10 Test report

The test report shall include the following particulars:

a) reference to this International Standard;

b) all details necessary for complete identification of the sample, including type, manufacturer's code number, trade name, etc.;

c) if the sample was in the form of a caprolactam solution (as opposed to solid caprolactam), the concentration of the solution (see 7.3);

d) any treatment of the sample prior to the determination;

e) the permanganate absorption number;

f) the date of the determination.

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